Using Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions from refineries and oil depots

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INTRODUCTION

Industrial volatile organic compound (VOC) emissions may contribute significantly to ozone formation[1]. In order to improve the understanding of their influence, a comprehensive emission study has been undertaken in the Los Angeles metropolitan area on behalf of the South Coast Air Quality Management district (SCAQMD). Gas emissions at six refineries and a tenfold tank farms and oil terminals were measured using several unique optical methods. The methods include the Solar Occultation Flux Method (SOF)[2,3] which is an optical remote sensing technique for quantifying fugitive VOC emissions from industrial sources. Measurements were carried out in September/ October 2015 in the Wilmington and Carson area (Los Angeles, California). The measurements in this study were quality assured by carrying out a controlled source gas release study and side by side measurements with several other techniques. In this presentation the used measurements methods and the main results from the field campaign will be discussed.

METHOD AND RESULTS

The methodologies and techniques used are shown in Table 1 with corresponding detection levels. In addition a short description of each technique is given and further information can be found in the report of a previous pilot study[4,5] or elsewhere[6]. The SOF (Solar Occultation Flux) method[2,3] is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. Using multivariate optimization it is possible from these solar spectra to retrieve the path-integrated concentrations (referred to as column concentrations), in the unit mg/m^2, of various species between the sun and the spectrometer. The measurements are carried out from a mobile platform making it possible to measure in a circle around leaking areas discriminating between upwind and downwind mass fluxes. The column measurements are combined with wind measurements to estimate the gas flux. In this study a wind LIDAR operated by SCAQMD was utilized.

Figure 1. In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by multiplication with the wind speed.

Mobile DOAS (Differential Optical Absorption Spectroscopy) measurements[7] of scattered solar light in zenith direction was carried out in parallel with the SOF measurements, from the same vehicle, to measure formaldehyde, NO_2 and SO_2. DOAS works in the ultraviolet (UV) and visible wavelength region while SOF works in the infrared region and hence there are large differences in spectroscopy and in the used spectrum evaluation methods. However, both methods measure vertical columns which are integrated along measurement transects and multiplied by the wind to obtain the flux. The principle of flux-measurements using Mobile DOAS is hence the same as for SOF, although it is not necessary to compensate for any slant angle observations since the telescope is always pointing towards zenith. The DOAS system also works under cloudy conditions in contrast to SOF, although the most precise measurements are conducted in clear sky.

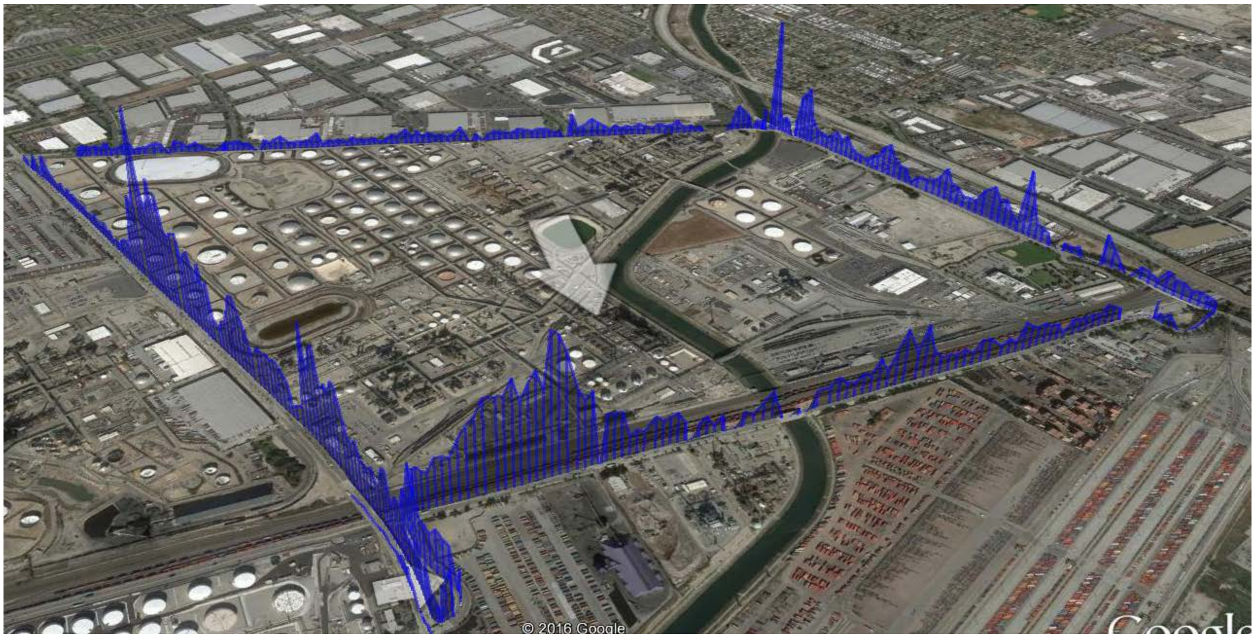
The column measurements using SOF were complemented by mobile extractive measurements using multi-reflection absorption cells in the infrared region (MeFTIR) or UV (Mobile White cell DOAS). Such extractive measurements have better speciation than the SOF measurements and by measuring the composition of various VOCs downwind the studied industries it is possible to infer emissions of more species than obtained by the SOF instrument alone, i.e. aromatic VOCs (BTEX) and methane. Here it is assumed that the ratio of BTEX versus alkanes that is measured on the ground represents the overall ratio in the emission plume. This may not be true, especially for the process area, and therefore the derived emission value is more uncertain. The extractive measurements were also complemented by tracer gas releases at the sources to estimate emissions independently from the SOF, using the tracer correlation approach[8]. In Figure 2 we show examples of SOF column measurement downwind an oil well area in Long beach (derricks and tanks). Measurements were also done at several refineries while the second one shows the corresponding data for an oil refinery.

Table 1 Techniques used with detection limits and parameters measured.

Parameter	**SOF**	**Mobile sky DOAS**	**Mobile Extractive FTIR (MeFTIR)**	**Mobile White cell DOAS (MW-DOAS)**
Compounds	Alkane,C_2H_4, C_3H_6, C_4H_8, NH_3	NO_2, SO_2 HCHO	Alkane,CH_4, C_2H_4, C_3H_6, C_4H_8	BTEX
Detection limit	0.1-5 mg/m^2	0.1-5 mg/m^2	1-10 ppb	0.2-3 ppb
Flux limit	0.2-1 kg/hr	1 kg/hr	0.2-2 kg/hr	1 -2 kg/hr
Meas. mode	Vert. Column	Vert. Column	Point Sample	Point Sample
Wind Speed	2-12m/s	2-12m/s	2-12m/s	2-12m/s
Time response	1-5 sec	1-5 sec	5-15 sec	1-30 sec
Typical accuracy in column and concentration measurement	3-5%	3-5%	3-5%	3-7%
Typical accuracy in flux estimate using wind LIDAR data	<25%	<25%	<25% (with tracer)- <35%*(with SOF)	<25% (with tracer)- <35%*(with SOF)
Complementary activity to obtain flux	Wind measurement from mast, and balloon, or LIDAR	Wind measurement from mast and balloon or LIDAR	For point sources tracer gas releases (N_2O, acetylene) For large sources, ratio measurements on the ground of pollutant X versus alkane. This value is multiplied by SOF alkane value to obtain a flux.	Operated in parallel with MeFTIR. For large sources, ratio measurements on the ground of pollutant X versus alkane. This value is multiplied by SOF alkane value to obtain a flux.

*Uncertainty depends if tracer gas is used

Figure 2. Example of a SOF column measurement downwind of a refinery in the Los Angeles metropolitan area in October 2015. The height of the staples corresponds to the relative amount of alkanes. The arrow corresponds to the wind flow.



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